PREPARATION OF NITROGEN CONTAINING HYDROCHAR BY HYDROTHERMAL CARBONIZATION OF WATER SPINACH AND SOY BEAN SPROUT WASTE

NURUL SYAZLIZA BINTI MOHD

UNIVERSITI SAINS MALAYSIA

2018

PREPARATION OF NITROGEN CONTAINING HYDROCHAR BY HYDROTHERMAL CARBONIZATION OF WATER SPINACH AND SOY BEAN SPROUT WASTE

by

NURUL SYAZLIZA BINTI MOHD

Thesis submitted in partial fulfilment of the requirement

for the degree of Bachelor of Chemical Engineering

June 2018

ACKNOWLEDGEMENT

First and foremost, I would like to convey my sincere gratitude to my supervisor, Professor Dr. Bassim H. Hameed for his precious encouragement, guidance and generous support throughout this work.

I would also extend my gratitude towards all the MSc and PhD students for their kindness cooperation and helping hands in guiding me carrying out the lab experiment. They are willing to sacrifice their time in guiding and helping me throughout the experiment besides sharing their valuable knowledge.

Apart from that, I would also like to thank all SCE staffs for their kindness cooperation and helping hands. Indeed their willingness in sharing ideas, knowledge and skills are deeply appreciated. I would like to express my deepest gratitude to my beloved parents Mohd bin Abdullah and Zaila binti Hamzah for their continuous love and support.

Once again, I would like to thank all the people, including those whom I might have missed out and my friends who have helped me to the accomplishment of this project. Thank you very much.

Nurul Syazliza binti Mohd

June 2018

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

HTC	Hydrothermal carbonization
HHV	Higher heating value
HTL	Hydrothermal liquefaction
HTG	Hydrothermal gasification
HT	Hydrothermal
APR	Aqueous phase reforming
EDX	Energy- disperse x-ray
FTIR	Fourier-transform infrared spectroscopy
SEM	Scanning electron microscopy

PENYEDIAAN HIDROCHAR YANG MENGANDUNGI NITROGEN MELALUI HIDROTERMA KARBONISASI DARI SISA KANGKUNG DAN SISA TAUGE

ABSTRAK

Hidroterma karbonisasi (HTC) adalah proses rawatan awal termokimia apabila biojisim dirawat pada keadaan suhu dan tekanan yang tinggi dan menghasilkan bahan berkarbon yang turut dikenali sebagai hidrochar. Hidrochar adalah salah satu pengganti ataupun alternatif untuk menggantikan arang. Bahan api fosil memerlukan ratusan hingga jutaan tahun untuk dihasilkan sementara hidrochar hanya memerlukan kurang dari 12 jam untuk dihasilkan. Sisa kangkung dan sisa tauge telah dipilih sebagai bahan asas dalam kajian ini kerana bahan tersebut merupakan salah satu sayur-sayuran yang mempunyai kadar pertumbuhan yang tinggi di Malaysia dan mudah didapati. Kangkung dan tauge adalah antara bahan utama dalam masakan di Malaysia. Di dalam kajian ini, proses HTC telah dibuat pada suhu 180 ^{o}C sehingga 200 ^{o}C selama dua hingga enam jam pada kadar pemanasan sebanyak 25 ^{o}C untuk seminit. Produk iaitu hidrochar yang dihasilkan ditapis dan dipanaskan di dalam ketuhar pada 105 ^{o}C untuk sehari . Keadaan yang terbaik untuk menghasilkan kadar pulangan produk tertinggi iaitu 44.60% adalah pada 180 ^{o}C selama enam jam. Sisa kangkung menghasilkan jumlah pulangan hidrochar lebih tinggi daripada sisa tauge iaitu 44.60% manakala sisa tauge pula 40.80% untuk kadar pulangan tertinggi. Hidrochar yang dihasilkan dicirikan menggunakan SEM, EDX dan FTIR untuk menunjukkan sifat hidrochar. Keputusan dari kajian ini menunjukkan sisa kangkung dan sisa tauge mempunyai potensi untuk penyediaan hidrochar menggunakan HTC.

PREPARATION OF NITROGEN CONTAINING HYDROCHAR BY HYDROTHERMAL CARBONIZATION OF WATER SPINACH AND SOY BEAN SPROUTS WASTE

ABSTRACT

Hydrothermal carbonization (HTC) is a thermochemical pre-treatment process where solid biomass is treated under hot compressed water to produce carbonaceous material called hydrochar which is coal-water slurry state. Hydrochar is one of alternatives in replacing coal which takes hundred to million years to be formed while hydrochar only require less than 12 hours to produce. Water spinach and soy bean sprouts are selected as the feedstock in this research because of their higher production potential in Malaysia can be easily attain as Malaysian dishes always contain both of these type of vegetables. In this study, hydrothermal carbonization was done from 180°C to 200°C for 2 to 6 hours residence time. Raw feedstock was fed into hydrothermal carbonization at heating rate of 25°C/min. The product obtained was filtered and dried in oven at 105°C for one day, forming hydrochar. The best conditions that producing the highest yield of hydrochar was 180°C and 6 hour of residence time which producing 44.60% hydrochar yield. Water spinach waste was producing higher hydrochar yield than soy-bean sprout waste which are 44.60% and 40.80% respectively for the highest yield obtained. The hydrochars were characterized using scanning electron microscope (SEM), energy- disperse x-ray (EDX) and fourier-transform infrared spectroscopy (FTIR) that shows the hydrochars properties. The results revealed that water spinach and soy-bean sprout waste were potential source for preparation of hydrochar by hydrothermal carbonization.

CHAPTER ONE

INTRODUCTION

Chapter one consists of four parts which are hydrothermal carbonization in producing hydrochar, problem statement, research objectives and scope of research. This chapter establishes the introduction, purpose, significance and scope of research for "Preparation of nitrogen containing hydrochar by hydrothermal carbonization of water spinach and soy bean sprouts waste". This chapter also introduces the significance of hydrothermal carbonization and hydrochar.

1.1 Hydrothermal Carbonization in Producing Hydrochar

Nowadays, utilizing clean and renewable energy is the major concern issue globally as the effect of shortage of fossil resources. Biomass is one of the important renewable source of energy as it is sustainable but, comparing biomass to other non-renewable energy such as coal, biomass has lower calorific value and high moisture content. Biomass is renewable energy source that have carbon in the structure unlike water, wind and solar. It is well known due to low-price feedstock, readily available and sustainable (Gao *et al.*, 2015). Although biomass is known with one of the most important renewable sources of energy, the physical and chemical properties of fuel produced is non-satisfying as it has low heating value, high moisture content and low bulk density. Pre-treatment of biomass is necessary before it is utilized as energy resource (Kambo and Dutta, 2015).

Biomass can be improved into liquid, solid and gaseous fuels using physical, chemical and biological conversion processes. Hydrothermal carbonization (HTC) is a thermochemical pre-treatment process where solid biomass is treated under hot compressed water to produce carbonaceous material called hydrochar which is coal-water slurry state (Li *et al.*, 2013) . Hydrochar has high energy density and the fuel value similar to lignite coal, low operation temperature and capable to handle wet feed which is preferable.

Hydrothermal carbonization process only requires less than 12 hours for the conversion of biomass into a material (hydrochar) similar to brown coal (Ramke *et al.*, 2009) while natural process requires hundred to million years that make it non-renewable sources as the period is too long. Even though direct combustion to biomass have less risk and cheaper, direct combustion is not a good option as it has high moisture, energy content and alkaline earth metal content (Liu and Balasubramanian, 2012). Conversion of solid biomass to hydrochar by hydrothermal carbonization process can reduce greenhouse gas emissions and using lower energy requirements for the conversion of wet feedstocks to compare with traditional waste conversion process (Berge *et al.*, 2015).

As the decreasing supply of fossil energy and the increasing environmental concerns, the biomass based energy is getting attention and gaining importance worldwide. There are several thermochemical processes such as pyrolysis, hydrogenation and gasification. The feedstock of hydrothermal carbonization do not require to be dried therefore, it require low energy in the process. Water spinach and soy bean sprouts wastes are more suitable feed for conversion by hydrothermal carbonization than other techniques because of the moisture content and lower temperature required.

HTC process will produce hydrochar which can be used for multiple purpose as energy sources, soil amendment processes and activated carbon adsorbents. Hydrochar is believed to have moderate calorific value, high aromaticity structures and mesoporous textures (He *et al.*, 2013). Hydrochar is applied in several fields which are environment, energy, adsorbent and medical field (Fang *et al.*, 2018). Hydrochar is known as feedstock for carbon fuel cells, soil fertility, soil amendment and adsorbent for harmful pollutants (Sun *et al.*, 2014) (Berge *et al.*, 2015).

1.2 Problem Statement

Demand for application of biomass-derived energy is increasing in importance due to decreasing supply of fossil fuels. Natural process in producing fossil fuels requires hundred to million years that make it non-renewable sources as the period is too long. Food waste signifies high percentage for municipal solid waste in Malaysia which is 8,000 tonnes of food per day and leading the composition of 45% or 15,000 tonnes of waste that end up at landfills in Malaysia (Chan, 2014). For fruits and vegetables, 20% to 50% is thrown away.

Water spinach and soy bean sprouts are selected as the feedstock in this research because of their higher production potential in Malaysia can be easily attain as Malaysian dishes always contain both of these type of vegetables. The fact of growing those two types of vegetables are easy, make it easier to obtain. Currently, government is only using conventional landfills and incineration methods in solving this problem (Lim *et al.*, 2016). Food waste is being disposed at landfills and this solution is not sustainable and created a lot of problem such as generates leachate, depletes landfill space and produces odour.

1.3 Research Objectives

The objectives for this research are to,

i) Prepare hydrochar from water spinach and soy bean sprouts waste using hydrothermal carbonization process.

ii) To characterize water spinach and soy bean sprouts as prepared hydrochars for their properties.

1.4 Organization of Thesis

There are five chapter in this report. The following are the contents for each chapter in this study.

Chapter 1 consists of four parts which are hydrothermal carbonization in producing hydrochar, problem statement, research objectives and scope of research. This chapter establishes the introduction, purpose, significance and scope of research.

Chapter 2 provide literature review and overview of previous research in this study. It consists of several part which are biomass, hydrochar, thermochemical treatment, hydrothermal method, hydrothermal carbonization and application of hydrochar.

Chapter 3 covers the experimental materials required, equipment, project management plan and experimental procedure in this study. This chapter provide detail description of equipment, materials used and procedure in this study.

Chapter 4 refers to the experimental results and discussions of the data obtained. This chapter provides further discussion on the influence of temperature and residence time to hydrochar yield and the characterization of hydrochar.

Chapter 5 concludes all the findings achieved in this study. Recommendations also included in this chapter for improvement for future studies on this topic.

1.5 Research Scope

In this study, water spinach waste and soy-bean sprout waste were collected from a market at Parit Buntar, Malaysia. After that, some of the waste will be dried in oven and shredded. The shredded dried waste will be characterized as the raw waste using EDX, FTIR and SEM. The characterization was done to observe and study the properties of both type of waste.

After that, 5 g of biomass will undergoes HTC in the reactor with different operating condition which are temperature at 180, 190 and 200 ^{o}C and residence time at 2, 4 and 6 hour respectively. These step was done to analysed the best operating condition for the highest yield for production of hydrochar. Hydrochar obtained will be characterized by EDX, FTIR and SEM to study the properties of hydrochar containing nitrogen produced.

CHAPTER TWO

LITERATURE REVIEW

This chapter provide literature review and overview of previous research in this study. It consists of several part which are biomass, hydrochar, thermochemical treatment, hydrothermal method, hydrothermal carbonization and application of hydrochar. In this chapter, the significant of biomass as energy resources and hydrothermal carbonization in producing hydrochar is discussed.

2.1 Biomass

Biomass is one of the most important energy resources. In worldwide rank for energy utilized, biomass ranks fourth which is approximately 14% of the world's energy demand while in developing countries, biomass ranks first which is approximately 35% (Hall *et al.*, 1992) . Biomass contribute a lot of benefit as a combustion feedstock because of high volatility of the fuel and the high reactivity of both the fuel and hydrochar but biomass contains fewer carbon and more oxygen to be compare with solid fossil fuels (Demirbas, 2004).

Biomass is renewable energy source that have carbon in the structure unlike water, wind and solar. It is well known due to low-price feedstock, readily available and sustainable (Gao *et al.*, 2015). Furthermore, biomass as energy resources can help in reducing the emissions of green-house gas because it is carbon neutral. Same amount of carbon dioxide is absorbs during the growth of biomass and releases during combustion of biomass (Demirbas, 2004). The dependence of fossil fuels as main energy resources also can be reduce if biomass is fully utilize (Novianti *et al.*, 2016).

Food waste signifies high percentage for municipal solid waste in Malaysia which is 8,000 tonnes of food per day and leading the composition of 45% or 15,000 tonnes of waste that end up at landfills in Malaysia (Chan, 2014). For fruits and vegetables, 20% to 50% is thrown away. Food waste is difficult to treat using old method such as combustion as food waste contain high content of moisture.

Despite all the benefit of utilizing biomass as energy resources, there is several problem need to be overcome to make sure it is effective. Raw biomass material need to undergo pre-treatment because it has high moisture content, hydrophilic and low bulk density (Novianti *et al.*, 2016) . Currently, combustion is mainly apply in conversion of biomass and leading at approximately 97% of the world's bio-energy production. By using chemical, physical and biological process, biomass can be transform into different state of fuel required which reducing cost for storage and easier to handle (Demirbas, 2004).

2.2 Hydrochar

Hydrochar is solid product that is obtained from hydrothermal carbonization. Combination of high heat and pressure converts biomass into a carbon dense material. Hydrochar has high energy density and the fuel value similar to lignite coal, low operation temperature and capable to handle wet feed (Steurer and Ardissone, 2015) . Hydrochar can be used for multiple purpose such as energy sources, soil amendment processes and activated carbon adsorbents.

Hydrochar can be obtained by two major reaction pathways. Firstly, hydrochar can be obtained by direct solid-solid conversion of biomass feedstock which undergoes devolatilization, intramolecular condensation, dehydration and decarboxylation reaction. Secondly, hydrochar can be formed by the transformation of intermediate product in aqueous phase which undergoes hydrolysis, dehydration, decarboxylation, polymerization and aromatization (Chen *et al.*, 2018). Both of reactions reduced the hydrogen and oxygen content but increased the carbon content in hydrochar (Zhao *et al.*, 2014).

There are two types of char which are biochar and hydrochar. Biochar, a stable carbon-rich solid, is produced by pyrolysis or gasification. Biochar and hydrochar can be used for the same purposes but their properties in terms of physical chemical are differ. The pH for biochar is more than 7 while for hydrochar is less than 7. Eventhough using same feedstock, hydrochar produced has lower carbon content than biochar (Sun *et al.*, 2014). Char yield that is obtain in producing biochar is 10-35% while more than 50% for hydrohar.

Hydrochar is believed to have moderate calorific value, high aromaticity structures and mesoporous textures (He *et al.* , 2013). Therefore, hydrochar has much lower ash content than biochar. Moreover, hydrochar contains reduced alkali , heavy metal content and an increased higher heating value (HHV) to compare with biochar (Kambo and Dutta, 2015) .

2.3 Thermochemical treatment

Thermochemical treatment of biomass which are gasification, pyrolysis and hydrothermal carbonization are effective method to convert biomass into valuable products (Wu *et al.*, 2017). Gasification and pyrolysis produce biochar while hydrothermal carbonization produce hydrochar. Gasification and pyrolysis generally require dry condition for reaction medium while hydrothermal carbonization prefer wet medium. This condition gives a big advantage in utilizing hydrothermal carbonization method as feedstock do not need to be dried before undergoes the process thus suitable for wet biomass feedstock.

Char yield for both gasification and pyrolysis is 10-35% which is less than char yield for hydrothermal carbonization (50%). Gasification is a process of partial combustion at high temperature, (850-900 ^{o}C), but short residence time (10-20 s). The product for gasification is synthetic gas. Gasification process will end up producing biochar in small amount which is less than 10% for char yield. Gasification process produce highly toxic biochar. Pyrolysis process is a thermochemical decomposition process that require 400-700 ^{o}C for temperature and long residence time. Hydrothermal carbonization require the lowest temperature among these 3 method which is 180-350 ^{o}C but long residence time (Ramke *et al.*, 2009).

2.4 Hydrothermal (HT) method

Hydrothermal treatment is a process to treat biomass with the presence of water at certain temperature and pressure. There is a lot of benefit in utilizing this treatment to compare with other biofuel production methods because it has high energy and separation efficiency, the flexibility to use mixed feedstock and the production of direct replacements for existing fuels (Zhao *et al.*, 2014). Moreover, as HT operate with high temperature, biofuels obtained will be free of biologically active organisms or compounds (Zhao *et al.*, 2014).

HT treatment consist of four main types which are hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), hydrothermal gasification (HTG) and aqueous phase reforming. Hydrothermal treatment combine heat and water to convert food waste into product as coal alternative while liquid part during this process can be used as organic fertilizer (8). The variation hydrothermal method is caused by different of processing conditions such as temperature, pressure, residence time, catalyst and solvent required.

Hydrothermal carbonization process require low temperatures (180-350 ^{o}C) and low pressures (below 2 MPa) with the presence of water producing product in solid form which is hydrochar. This process only requires less than 12 hours for the conversion of biomass into hydrochar (Ramke *et al.*, 2009). This process is not operate with harsh conditions such as high temperature and pressure, requirement of catalyst or strong acids and long reaction times.

Hydrothermal liquefaction process require intermediate temperatures (280-370 ^{o}C) and high pressures (10- 25 MPa) with the presence of water producing product in liquid form which is bio-fuel. Residence time in this process is 5-30 min for the conversion of biomass into bio-fuel.

Hydrothermal gasification process require high temperatures (300-700 ^{o}C) and high pressures (13.5- 25 MPa) with the presence of catalyst producing product in gas form which is hydrogen gas. This process only requires 1-120 min for the conversion of biomass into hydrogen gas. Alkali with H_2O_2 and Trona catalyst are required and act as catalyst during this process. Aqueous phase reforming (APR) process require intermediate temperatures (220-250 ^{o}C) and low pressures (1.5 – 5 MPa) with the presence of catalyst producing product in gas form which is hydrogen and methane gas. This process only requires 4-6 hours for the conversion of biomass into hydrogen and methane gas. Nickel and platinum are required and act as catalyst during this process.

HT treatment is believed can upgrade low value resources such as low rank coal, municipal solid waste and food waste. Not only that, HT treatment also produce processing liquid which is high in nutrients therefore, it is suitable to fertilizer the crops (Novianti *et al.*, 2016). HT treatment is certainly a promising way to transform the biomass as it have several types of treatment that can be operate with the suitability of condition for the feedstock and requirement.

2.5 Hydrothermal carbonization (HTC)

Hydrothermal carbonization (HTC) is a thermochemical pre-treatment process where solid biomass is treated under hot compressed water to produce carbonaceous material called hydrochar which is coal-water slurry state. HTC process is known to be natural process which is the coalification of organic material in aqueous phase at high temperature and pressure (Ramke *et al.*, 2009). HTC is also known as wet torrefaction. In 1913, Bergius made an attempt of converting cellulose into synthetic coal which is the initial concept for hydrothermal carbonization. HTC is one of the favorable thermochemical processing for producing hydrochar (Reza *et al.*, 2014).

Hydrothermal carbonization is based on a simple chemical process (Ramke *et al.*, 2009) :

$$C_6H_{12}O_6 \rightarrow C_6H_2O + 5H_2O + \sim 950\frac{\mathrm{kJ}}{\mathrm{mol}} \quad (2.1)$$

Based on Equation 2.1, hydrothermal carbonization is exothermic as energy is released during this process therefore, energy required for the conversion can be obtained and possibly surpassed (Ramke *et al.*, 2009). Moreover, during HTC process, aqueous by-product is easily separated from hydrochar (He *et al.*, 2013).

HTC has been known as wet process that required moisture as heating medium. It is one of effective methods for biomass conversion as char yield can be more than 50%. This method has lower energy consumption as temperature and required is low. The phase change from water to steam during this method is largely evaded therefore, it can reduce energy required. Feedstock for hydrothermal carbonization do not require to be dried therefore, this process demand lower energy. In this method, water is used as solvent and catalyst which is more economical and safe (Chen *et al.*, 2018). HTC is believed as capable method as wet biomass conversion (Toufiq Reza *et al.*, 2016).

The condition of this process which is reaction temperature and pressure, increase the ionization of water, causing a high concentration of acidic hydronium ions and hydroxide ions (Kambo and Dutta, 2015). The hydronium ions are then saturate with the organic components, which overturns the radical polymerization and improves cleavage of hydrogen bonds. This cause water solvent increases the hydrolysis reaction during HTC process. Therefore, without pre-drying process, wet biomass can still be utilized directly (Chen *et al.*, 2018).

This method required feedstock such as food waste or plant-based product and placed in a pressure vessel with the presence of water at certain range of temperature (180-350 ^{o}C) and the pressure is below 2 MPa. This process is applicable to wet biomass because high pressyre is applied during this process and cause water to not evaporate. The reactor is closed over 2-12 hour period. After the reactor is cooled down and opened, black watery fluid is obtained. After filtered and dried at 105 ^{o}C for 24 hour, hydrochar is formed. The HTC process produce three product which are hydrochar (solid form), bio-oil mixed with water (liquid form) and small amount of gases which is largely carbon dioxide (Kambo and Dutta, 2015).

HTC process is environmentally friendly because this process does not produce any hazardous chemical waste (Xue *et al.*, 2012).

2.6 Application of hydrochar

Hydrochar is applied in several fields which are environment, energy, adsorbent and medical field (Fang *et al.*, 2018). Hydrochar is known as feedstock for carbon fuel cells, soil fertility, soil amendment and adsorbent for harmful pollutants (Sun *et al.*, 2014).

The main application of hydrochar is energy sources. Hydrochar can be used directly as a solid fuel. Besides, hydrochar is used to produce fuel cells, electrode supercapacitors, and batteries as a medium for converting and storing energy (Fang *et al.*, 2018). In capacitor, hydrochar was combined with nickel in order to increase the specific capacity of hydrochar by approximately 149% (Ding *et al.*, 2012). Hydrochar can be used as the material in capacitor to reduce the production cost.

Hydrochar is cheap adsorbents which is used for the removal of heavy metals, organics, phosphate and pathogens (Fang *et al.*, 2018). The capacity for sorption ability is based the production condition and type of feedstock. Hydrochar can be modify with chemical substance such as potassium hydroxide and hydrogen peroxide to increase their sorptive abilities for heavy metals (Xue *et al.*, 2012).

For medical applications, silk hydrochar is used to produce quantum dots as suitable replacement for dyes. Florescent quantum dots are used for detection of disease at cellular level by medical imaging. Hydrochar is chosen as a suitable material because it has low toxicity, high cellular uptake and effective (Fang *et al.*, 2018).

Hydrochar can be added to soil to improve the effects of fertilizer even though most types of hydrochar especially hydrochar that is produced from plant biomass, have a low nutrient content. In order to increase the efficiency of fertilizer, nutrients from fertilizer are sorbed into pores of on the surface of the char material and then, hydrochar will gradually release the nutrients into the soil for plant (Bargmann *et al.*, 2014). Therefore, fertilizer required for each plant can be reduce.

CHAPTER THREE

METHODOLOGY

Chapter 3 covers the experimental materials required, equipment, project management plan and experimental procedure in this study. This chapter provide detail description of equipment, materials used and procedure in this study.

3.1 Research Plan

The overall experimental activities carried out in this study are presented in Figure 3.1.

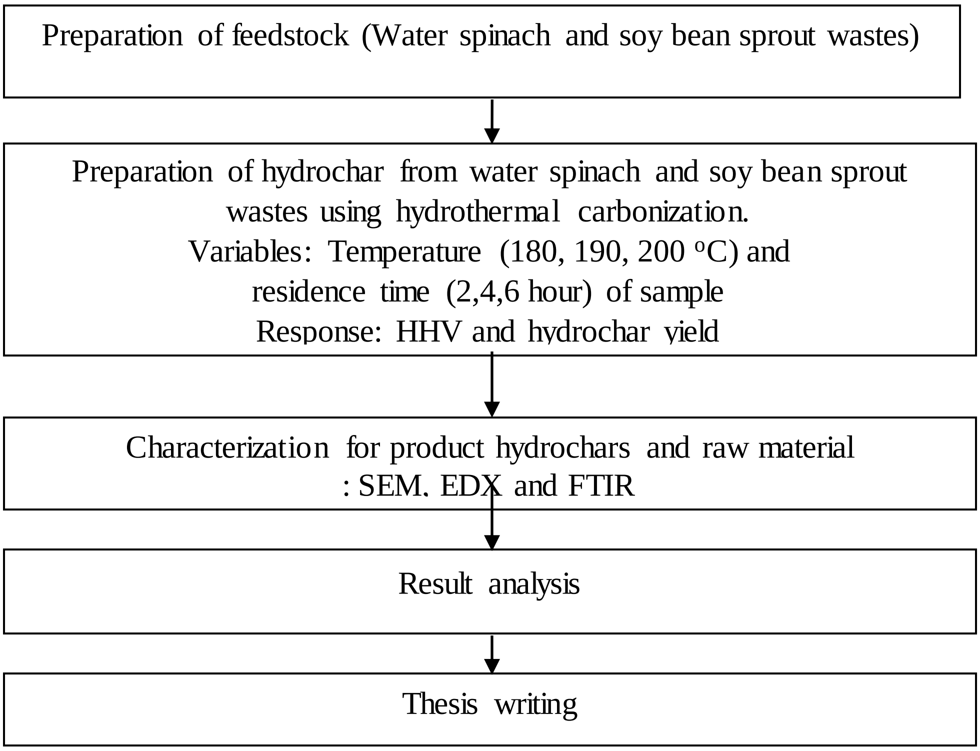

Figure 3.1 Schematic flow diagrams of experimental activities

3.2 Materials

In this study, water spinach waste and soy bean sprout waste were used as feedstock for preparation of nitrogen containing hydrochar by hydrothermal carbonization. There are two condition of sample which are wet and dry. For dry sample, water spinach and soy bean sprout are dried in oven at 105 ^{o}C for 24 hour and crushed into smaller pieces.

Figure 3.2 : Wet water spinach waste

Figure 3.3 : Wet soy bean-sprout waste

Figure 3.4: Dry water spinach waste

Figure 3.5 : Dry soy bean-sprout waste

3.3 Description of Equipment

Oven and grinder were used to prepare dried soy-bean sprout and water spinach. In hydrochar preparation, hydrothermal reactor was used to heat feedstock at 180, 190 and 200 ^{o}C for 2, 4 and 6 hour. After that, oven was used to dry the hydrochar at 105 ^{o}C for 24 hour. Finally, energy- disperse x-ray spectroscopy (EDX) is used to identify elemental composition of materials in hydrochar. Fourier-transform infrared spectroscopy (FTIR) is also used to obtain an infrared spectrum of absorption or emission in order to obtain chemical properties of sample. Lastly, scanning electron microscopy (SEM) to obtain the image for the surface morphology of activated carbon of the sample . The list of equipment and its general use is tabulate in Table 3.1 below.

Table 3.1: List of equipment

Equipment	Purpose
Oven	Drying water spinach and soy-bean sprout Drying hydrochar.
Grinder	Grind dried water spinach and soy-bean sprout into smaller size
Hydrothermal reactor	For hydrothermal carbonization process
EDX	To identify elemental composition of materials in hydrochar
Thermos-gravimentric analysis	To obtain ash content, moisture, volatile matter and fixed carbon of hydrochar
Scanning electron microscope	To examine the surface morphology of activated carbon
FTIR spectrometer	To characterize and identify the functional group of the samples

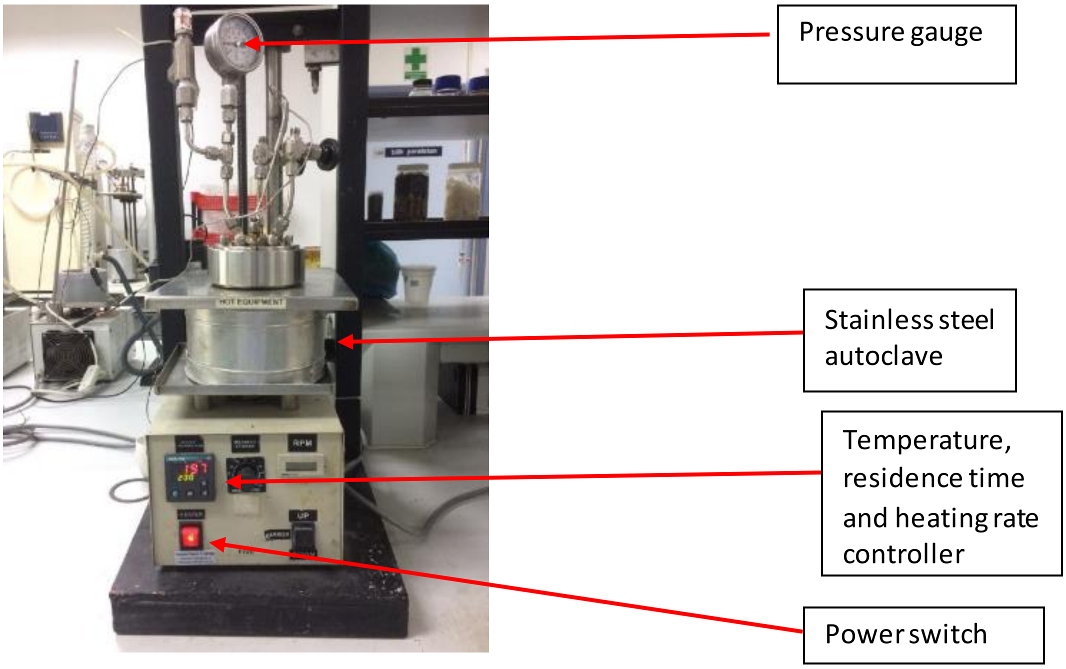

Figure 3.6 : Hydrothermal reactor

3.4 Experimental Procedure

3.4.1 Hydrochar Preparation

In this study, water spinach and soy bean sprout were used as feedstock for preparation of nitrogen containing hydrochar by hydrothermal carbonization. The feedstock was obtained from supermarket located near Universiti Sains Malaysia Kampus Kejuruteraan and prepared in two condition which are wet and dry. For dry sample, feedstock was oven dried at 105 °C for 24 h to expel the inherent moisture and grinded to smaller pieces. HTC process is performed in a hydrothermal reactor at their isobaric pressures of 16-40 bar. For each run, 5 g of biomass will feed into hydrothermal reactor. The reactor was heated at 180, 190 and 200 °C. The residence time were at 2, 4 and 6 hours. After the sample is cooled down to room temperature, the gas product is released to the atmosphere while solid and liquid product were separated by filtration. The hydrochar was left to dry in the oven at 105 °C for 24 hours. The weight of sample is then taken as W_2.

3.4.2 Characterization of Hydrochar

The raw biomass and hydrochar were analysed using EDX to identify elemental composition of materials. Fourier-transform infrared spectroscopy (FTIR) was also used to obtain an infrared spectrum of absorption or emission in order to obtain chemical properties of sample. Lastly, scanning electron microscopy (SEM) used to obtain the image for the surface morphology of activated carbon of the sample. Oxygen content was calculated by difference and higher heating value (HHV) using Dulong's equation (Elaigwu and Gillian M. Greenway, 2016) .

$$\text{HHV} = (0.3383 * \%\ \text{Carbon}) + (1.422 \times \%\ \text{Hydrogen}) - (\frac{\%\ \text{Oxygen}}{8}) \qquad (3.1)$$

The hydrochar yield was determined as the ratio of the produced hydrochar weight before placing it in the reactor and after drying (Elaigwu and Gillian M. Greenway, 2016).

$$\text{Hydrochar Yield } (\%) = \frac{W_2}{W_1} \times 100 \qquad (3.2)$$

$$W_1 = \text{dry weight of sample}$$

$$W_2 = \text{hydrochar weight}$$

Collected data were used to calculate hydrochar yield, moisture content, energy content and composition of carbon hydrogen and nitrogen content. The scanning electron microscope (SEM) were used to examine the surface morphology of activated carbon while FTIR spectrometer is important to characterize and identify the functional group of the samples.

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter shows the experimental results obtained and its related discussion consists of three main sections. The first part shows the study of hydrochar yield at different temperature while the second part dhows the relationship of hydrochar yield and residence time. Finally the characterization of the hydrochar samples were studied during the final part of this chapter.

4.1 The effect of temperature on hydrochar yield

Figure 4.1 shows hydrochar yield as a function of hydrothermal temperature for water spinach and soy-bean sprout. Temperature have important role in the hydrochar yield and showing same trends of hydrochar yield vs. temperature were observed for water spinach and soy bean sprout at 2 hour of residence time. As it can be seen decreasing the temperature from 180 to 200 ^{o}C resulted in an increase of hydrochar yield decreased rapidly with increasing temperature. Hydrochar yield for dry water spinach at 180 ^{o}C for 6 hour of residence time has the highest yield which is 44.60%. Dry feed shows higher hydrochar yield as shown for dry water spinach and wet water spinach because of the moisture level of wet water spinach that contribute to this result. In contrast, higher energy is require to dry the feed in order to obtain higher hydrochar yield.

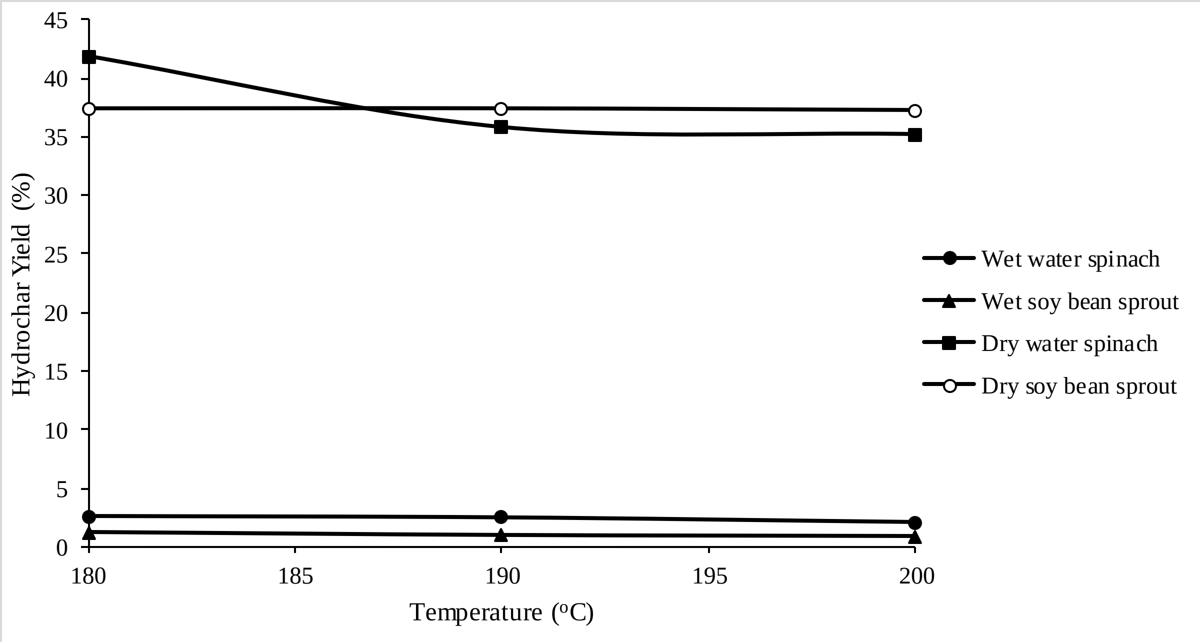

Figure 4.1 : Effect of temperature on hydrochar yield

Figure 4.2 shows hydrochar yield as a function of temperature for dry water spinach. In this graph, it can be seen that as temperature is increases, hydrochar yield is decreasing for 2, 4 and 6 residence time. This graph shows that hydrothermal temperature gives significant effects on the result of hydrochar yield.

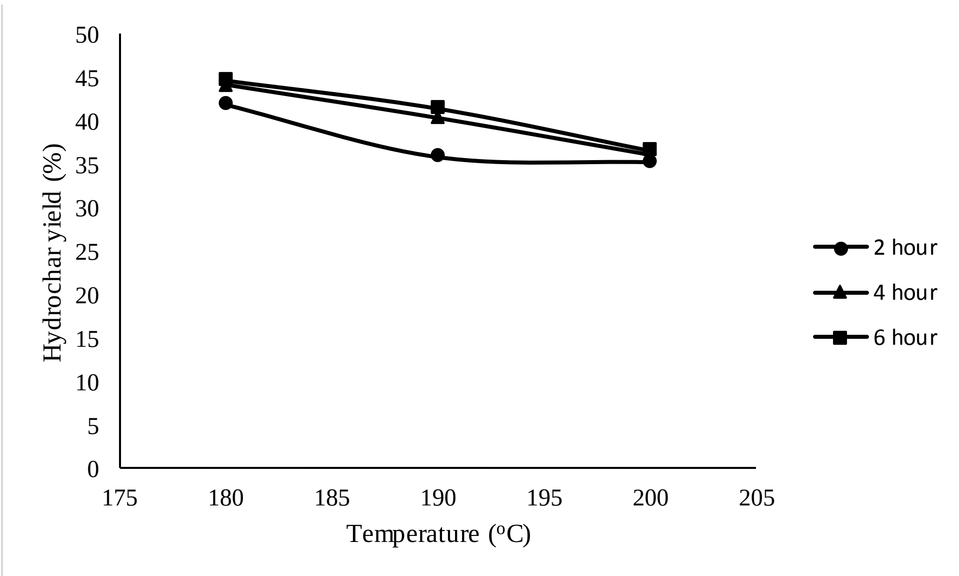

Figure 4.2 : Effect of temperature on hydrochar yield for dry water spinach

4.2 The effect of residence time on hydrochar yield

Figure 4.2 shows the influence of residence time on hydrochar yield at 180°C for water spinach nd soy-bean sprout. Residence time of 2 -6 hour showed same trends of hydrochar yield vs residence time at 180°C for water spinach and soy bean sprout. As it can be seen the longer the residence time, resulted in an increase of hydrochar yield increased rapidly with the increasing residence time. Based on figure 4.2, the highest hydrochar yield obtained is for dry water spinach at 180°C for 6 hour of residence time which is 41.80%. The longer the residence time, cause the higher requirement of energy in hydrothermal reactor. The large gap between dry and wet feed can be seen in Figure 4.2 because of the difference of moisture level of feed.

Hydrochar yields ranged from 35.2%-44.6% for dry feed while 0.9%-2.6% for wet feed. The largest yield is obtain the highest hydrochar yield obtained is for dry water spinach at 180°C for 6 hour of residence time which is 44.60%.

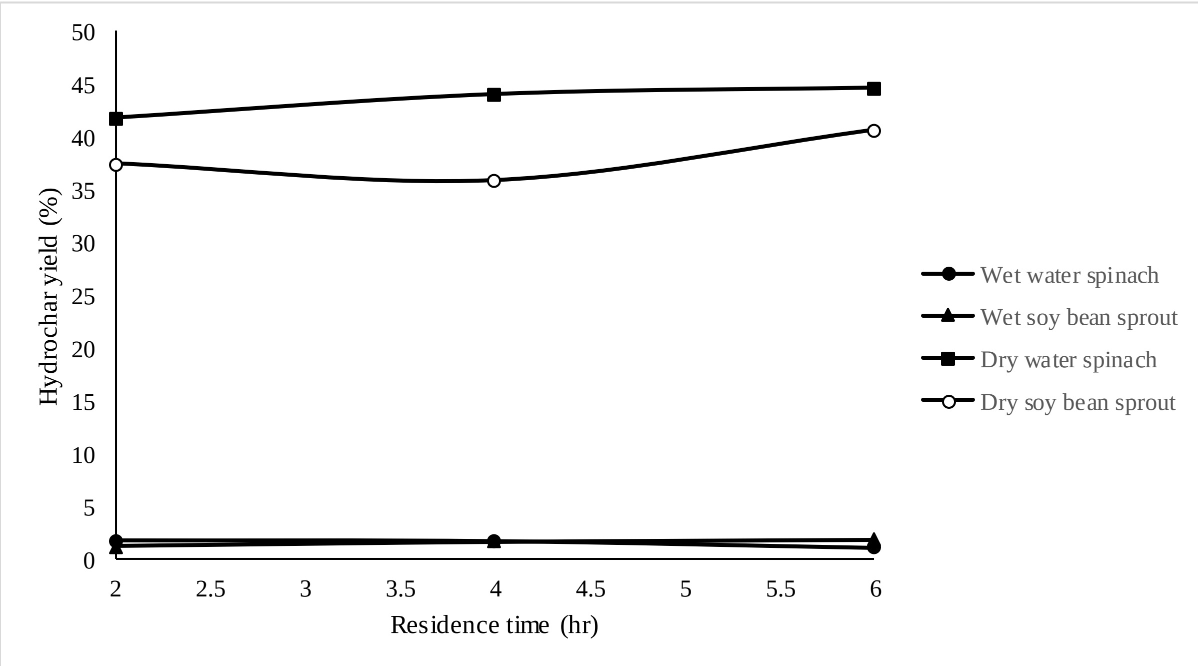

Figure 4.3 : Effect of residence time on hydrochar yield

Figure 4.4 shows the relationship of residence time and hydrochar yield for dry water spinach. It can be seen that when residence time is increases, hydrochar yield for dry water spinach will also increases.

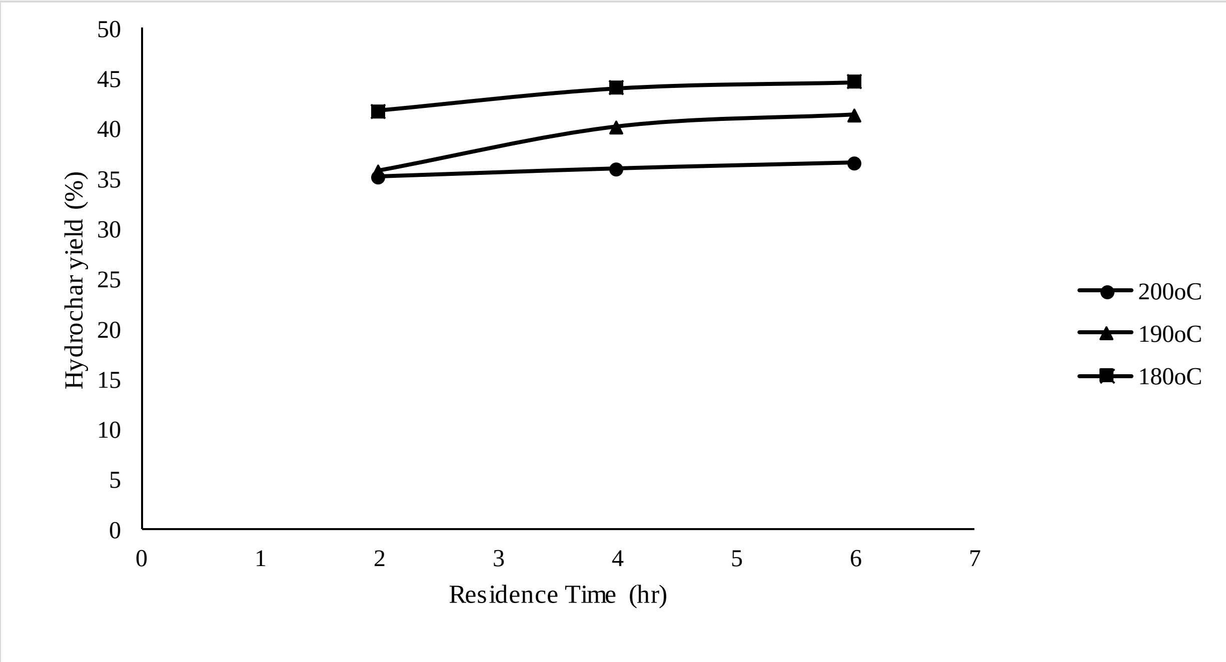

Figure 4.4 : Effect of residence time on hydrochar yield for dry water spinach

4.3 Characterization of Hydrochar

4.3.1 Optical Description

Figure 4.5-4.8 shows hydrochar from different biomass feed which are wet water spinach, wet soy-bean sprout, dry water spinach and dry soy-bean sprout. As it can be seen, hydrochar is in brown colour despite of different feed. The initial mass biomass feed for every hydrochar is 5g but the resulting mass of hydrochar which is affected by several conditiont and contribute to the different of hydrochar yield.

Figure 4.5 : Hydrochar from wet water spinach sprout

Figure 4.6 : Hydrochar from wet soy-bean

Figure 4.7 : Hydrochar from dry water spinach sprout

Figure 4.8 : Hydrochar from dry soy bean

4.3.2 Properties of biomass and hydrochar

Table 4.1 shows the elemental composition of dry water spinach, dry soy-bean sprout and hydrochars that were assessed using energy- disperse x-ray. As it can be seen, hydrochar produce contain a small composition of nitrogen while hydrochar from wet soy-bean sprout was not contain any nitrogen.

Table 4.1 : Proximate analyses of sample by EDX

	C (%)	O (%)	N (%)	S (%)	Mg (%)	Al (%)	P (%)	K (%)	Na (%)	Si (%)	Ca (%)	C/N ratio	O/C ratio
Dry water spinach waste	49.81	43.60	-	0.29	0.24	0.45	0.16	3.78	0.69	0.37	0.60	-	0.88
Hydrochar for wet water spinach	51.38	37.72	3.92	0.69	-	0.29	3.81	0.28	-	0.28	1.64	13.11	0.73
Hydrochar for dry water spinach	63.84	30.16	3.39	0.23	-	0.57	-	0.35	-	0.63	0.82	18.83	0.47
Dry soy bean sprout waste	56.56	41.35	-	0.17	0.24	0.12	0.51	1.06	-	-	-	-	0.73
Hydrochar for wet soybean sprout	63.54	36.10	-	0.36	-	-	-	-	-	-	-	-	0.57
Hydrochar for dry soy-bean sprout	64.99	31.99	2.79	0.22	-	-	-	-	-	-	-	23.29	0.49